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Passaic Valley Sewerage Commissioners

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FINAL REPORT

ON

THE PHASE I METALS SAMPLING AND ANALYSIS PROGRAM FOR THE NEW JERSEY COMPONENT OF THE NEW YORK/NEW JERSEY HARBOR ESTUARY PROGRAM

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EXECUTIVE SUMMARY

In 1990, the area encompassing the New York/New Jersey Harbor was declared impaired by the Environmental Protection Agency (EPA) under the provisions of the Clean Water Act, due to apparent water-quality criteria exceedances for particular metals. As a consequence of projected exceedances, EPA concluded that a point-source discharge control strategy was needed to establish discharge limits for metals being discharged to the Harbor, based upon total maximum daily loads (TMDLs) and waste load allocations (WLAs). Because of unreliable metals data for the major New Jersey tributaries, further sampling was mandated for four metals at five locations as part of Phase I of this two phased study.

The water samples were collected from the Hackensack, Passaic, and Raritan Rivers, and from Newark and Raritan Bays, and analyzed the following parameters: dissolved and total recoverable copper, nickel, lead, and mercury; total suspended solids (TSS); turbidity; dissolved organic carbon (DOC); particulate carbon (PC); particulate nitrogen (PN); pH; and salinity. Sediment samples were also collected at these same locations and analyzed for the following parameters: total recoverable metals (copper, lead, nickel, and mercury); fine grain metals; acid volatile sulfides (AVS); and simultaneously extracted metals (SEM).

The measured ambient concentrations of copper and lead never exceeded their respective water quality standards (WQS) at any of the locations; consequently, the log probability distributions projected that the ambient metals concentrations would not exceed the chronic WQS. The measured nickel concentrations exceeded the WQS once in the Hackensack River, and were within 2 $\mu\text{g/L}$ of the WQS in five other instances; consequently, the log probability distribution projected an exceedance of the chronic WQS for nickel in the Hackensack River. On the Passaic River the probability distribution indicated that the WQS was nearly projected to be exceeded. Mercury levels did not exceed the WQS in Raritan Bay, but there were four occasions when the WQS was exceeded in the Raritan River, and for Newark Bay, the Hackensack and Passaic Rivers collectively, the mercury WQS was exceeded on all but four sampling dates. Consequently, with the exception of Raritan Bay, the log probability distributions projected that the chronic WQS would be exceeded for all other locations.

There were no statistically significant differences between the ambient concentrations of the four metals measured during the rainfall events, and the concentrations measured during dry periods.

There were also no statistically significant differences between the measured concentrations of the four metals for samples collected over a complete tidal cycle.

All four metals were analyzed from the sediment samples collected at the same five stations where the water samples were collected. Copper levels ranged from 66.9 - 176 $\mu\text{g/g}$, nickel levels ranged from 22.9 - 53.1 $\mu\text{g/g}$, lead levels ranged from 55.9 - 330 $\mu\text{g/g}$, and mercury concentrations ranged from 0.076 - 4.81 $\mu\text{g/g}$. There was a clear relationship between mercury sediment concentrations and ambient mercury concentrations, leading to the conclusion that high mercury concentrations in the sediments could be contributing to mercury concentrations in the water column.

In spite of the fact that a number of water quality criteria exceedances were projected for the New Jersey tributaries and Raritan and Newark Bays based upon the 1991 survey data, the more comprehensive data set collected in 1995 demonstrated relatively few potential water quality criterion exceedances, with the exception of mercury. Mercury was a problem at all but one station (Raritan Bay), and nickel was a problem on the Hackensack River and a potential problem on the Passaic River.

INTRODUCTION

In 1990, the area encompassing the New York/New Jersey Harbor was declared impaired by the Environmental Protection Agency (EPA) under the provisions of the Clean Water Act, due to apparent water-quality criteria exceedances for particular metals. Prior to 1990, surveys of the New York and New Jersey tributaries identified four metals (copper, nickel, lead, and mercury) that exceed water quality criteria at certain locations throughout the Harbor. As a consequence, EPA concluded that a point-source discharge control strategy was needed to establish discharge limits, based upon total maximum daily loads (TMDLs) and waste load allocations (WLAs), for these metals being discharged to the Harbor.

The development of the TMDLs is dependent upon the availability of high quality ambient data and load data. Data of sufficient quality were available for the New York side of the Harbor, and were used by EPA to develop and calibrate a model for the New York portion of the Harbor based on log probability distributions for projected ambient metal concentrations. The model was used to predict, at the appropriate duration and frequency, whether or not water quality criteria are being exceeded throughout the Harbor. Meaningful water quality exceedances were projected for the three major New Jersey tributaries (the Passaic River, the Raritan River, and the Hackensack River) for copper, nickel, lead, and mercury, but EPA recognized these projected exceedances may have been unrealistically high because they were based on an insufficient amount of high quality data for the metals in question for the New Jersey portion of the Harbor. Therefore, data of comparable quality to the New York data were needed for the New Jersey portion of the Harbor to finalize the model for the entire system, which is the subject of this report.

This monitoring and analysis program, commonly referred to as "database enhancement," was performed by Great Lakes Environmental Center (GLEC) on behalf of the New Jersey Harbor Discharger's Group (NJHDG). The study involved the collection of ambient water column data to accurately determine whether the metals copper, nickel, lead and mercury are present at levels exceeding water quality standards in the three New Jersey tributaries, plus Raritan and Newark Bays.

Based on the results of this program (Phase I), certain metals and/or tributaries may require additional monitoring to better understand the ambient concentrations and metal sources (Phase II).

For this program, all metals monitoring was executed using "clean metals techniques" for both sampling and analysis. Only data collected using "clean metals techniques" were considered acceptable, because all other metals data are potentially artificially high due to sample contamination and salt water matrix interference. Phase II will involve more extensive load and ambient sampling to collect data which will be used to finalize the calibration of the water quality model for the Harbor. Plans for implementation of the second phase will be finalized after the New Jersey dischargers, EPA, and the New Jersey Department of the Environment (NJDEP) have evaluated the data.

METHODS

For this phase of the program, one station each in the Hackensack, Passaic, and Raritan Rivers, and in Raritan and Newark Bays was sampled approximately twice per month for six months. The station locations correspond to sites which were tentatively identified by the water quality model as having water column exceedances for the metals of concern. The 12 sampling events included 3 wet weather events and 2 tidal cycle events (wet weather is defined as a rain event with more than ¼ inch of precipitation measured at Newark Airport; tidal cycle sampling involved the collection of 4 samples over the course of 1 tidal cycle). Samples were taken near mid-channel of each water body, and near the bottom of the water column, because previous studies have demonstrated higher concentrations of metals close to the bottom, in comparison with concentrations near the surface.

Each tidal cycle sampling event resulted in the collection of a total of four water samples: one at slack before ebb, one at slack before flood, one at maximum current when the tide was going out, and one at maximum current when the tide was coming in. For all non-tidal cycle sampling events, a single water sample was collected. In addition to collecting the water samples, one set of sediment samples was collected at each site over the six month period. In summary, there were a total of 90 water samples and 5 sediment samples collected in 12 sampling events over the six month study period:

- Three wet weather sample events x one water sample per event x five stations = 15 wet weather water samples.

- Two tidal cycle sample events x four water samples per event x five stations = 40 tidal cycle water samples.
- Seven dry weather events x one water sample per event x five stations = 35 dry weather water samples.
- One sediment sampling event x one sample per event x five stations = 5 sediment samples.

The water samples were analyzed by Battelle Ocean Sciences for the following parameters: dissolved and total recoverable copper, nickel, lead, and mercury; total suspended solids (TSS), performed both by filtering the sample with a nucleopore filter and by filtering the sample with a glass fiber filter (two separate analyses); turbidity; dissolved organic carbon (DOC); particulate carbon (PC); particulate nitrogen (PN); pH; and salinity.

The sediment samples were analyzed for the following parameters: total recoverable metals (copper, lead, nickel, and mercury); fine grain metals (prepared by filtering the sample with a 75 micron filter); acid volatile sulfides (AVS); and simultaneously extracted metals (SEM).

The data which were obtained from the Phase I monitoring were used by GLEC to develop log probability distributions each tributary for each metal that was measured. These probability distributions were then used to determine which tributaries are likely to experience criteria exceedances, and for which metals. Based upon these data, the Phase II monitoring strategy (the specific metals to be measured and the locations for metals measurements, if needed) will be determined in conjunction with EPA and NJDEP.

Tributary Water Column Surveys

Station Locations

One station in each of the five areas illustrated in Figure 1 was sampled on the dates presented in Table 1. One depth per station was sampled. The station locations were in Raritan Bay (Station #155), the Raritan River (Station #156), Newark Bay (Station #301), the Hackensack River (Station #303), and the Passaic River (Station #306). A 22 foot aluminum river boat was used to conduct the tributary sampling.

Navigation

Global positioning system (GPS) navigation was used to locate/relocate stations. The sampling vessel was anchored on station to collect continuous profiles of standard water quality parameters, and to collect the water samples for subsequent laboratory analysis.

Hydrographic Data Acquisition and Sample Collection

Hydrographic data were collected from vertical profiles with *in situ* conductivity/temperature/depth (CTD) instrumentation. The information returned from the *in situ* sensors controlled the collection of discrete water samples described below. During each hydrocast, the following *in situ* measurements were made:

- Conductivity
- Temperature
- Depth of sensors/water sample
- Dissolved oxygen (DO)
- pH
- Optical beam transmittance

Salinity and sigma-t (density at atmospheric pressure) were calculated from the conductivity and temperature. Hydrographic profiles were conducted from near-surface to within approximately 1 meter of the bottom. Navigational position and time were measured concurrently, and were recorded in the same data file.

Samples for metals analysis were collected at a depth 1 meter above the sediment surface using a 12-VDC peristaltic pumping system similar to that described in EPA Method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA, 1995). Samples for dissolved metal measurements were filtered with an in-line 0.45 micron filter; unfiltered samples were collected with the same system (after removal of the filter) for measurement of total recoverable metals, TSS, PC, PN, and DOC.

Metals samples were collected and stored in precleaned 0.5 and 1 liter Teflon and polyethylene bottles and preserved with high purity nitric acid. Samples for TSS determinations were collected in

1 liter polyethylene bottles. An aliquot of the water was syringe-filtered in the field through precleaned glass fiber filters (GF/F) and stored in glass vials for DOC analysis. Particulates collected on the GF/F were stored in foil for the PC and PN measurement. Samples for TSS, DOC, and PC determinations were stored on ice for transport to the laboratory (within 24 hours).

Samples collected for metals analysis were processed and analyzed using "clean techniques" to minimize the likelihood of sample contamination. Ancillary parameters were measured using routine laboratory methods.

Sediment Survey

Station Locations

Sediment samples were collected from the same locations the water column measurements were made during the period July 23 - 27, 1995. The sediment collections were performed following the water sample collections on those dates.

Navigation

As with water column sample collection, GPS navigation was used to locate/relocate the stations. The sampling vessel was anchored on station in order to collect the sediment samples needed for analysis.

Sample Collection

A Van Veen grab sampler (0.5 m²) was used to collect surface sediment for analysis of AVS/SEM, and total copper, nickel, lead, and mercury. The surface sediment was carefully removed using Kynar coated (Teflon) scoops, and placed in appropriate containers. To be consistent with studies previously conducted in the Harbor, the surface (0-5 cm) sediment was homogenized prior to chemical analysis. Homogenization took place in a glove bag under nitrogen, to prevent sulfide oxidation, and split for AVS/SEM and total metals analyses.

Total copper, nickel, lead, and mercury were measured using acid digestion/graphite furnace atomic absorption and/or inductively coupled plasma atomic emission and cold vapor techniques.

AVS was measured using GC techniques as outlined in Cutter and Oates (1987). SEM (Copper, Nickel, and lead) was measured using inductively coupled plasma-mass spectrometry.

Analysis of Water Quality Data

The metals data generated in this study are most relevant when they are compared with the respective ambient water quality criterion for each metal. Ambient water quality criteria are numerical criteria which have been developed by EPA to protect aquatic life and human health, and are threshold concentrations which, if they are not exceeded in the environment should not be harmful to freshwater and marine life and to human health. There are both acute and chronic water quality criteria; acute criteria are threshold concentrations which should not be exceeded at any time in the environment because mortality to aquatic life could be the consequence. Chronic criteria are typically lower than acute criteria, and are designed to protect aquatic life and human health against chronic, or ecologically damaging effects (growth, reproduction and long-term survival). Chronic water quality criteria are concentrations which can be exceeded under certain circumstances for short periods of time, but which cannot be exceeded in the environment for extended periods of time without affecting the integrity of the waterbody as a whole.

Most water quality criteria are expressed as dissolved metal, because it is the dissolved fraction that has been shown to be toxic to fish and invertebrates living in the water column; water quality criteria for copper, nickel and lead are examples of metal criteria that are expressed as dissolved metal. For some other metals (like mercury), the water quality criterion is based upon total recoverable metal because the primary concern for those metals is bioaccumulation and human health, rather than acute or chronic toxicity to organisms in the water column; the water-quality criterion for mercury is therefore expressed as total recoverable mercury. The relevant water quality criteria for the metals investigated in this study are: 5.6 $\mu\text{g/L}$ (dissolved) for copper, 8.2 $\mu\text{g/L}$ (dissolved) for nickel, 8.1 $\mu\text{g/L}$ (dissolved) for lead, and 0.025 $\mu\text{g/L}$ (total recoverable) for mercury.

Log probability distributions were used to determine if ambient metals concentrations could be expected, over time, to exceed the chronic water quality standard (WQS). The following steps were taken to calculate the log probability distributions for each metal at each site:

- 1) For the two tidal sampling events, the highest level measured from the four tidal cycles (ebb, flood, low, high) was used to represent the result for that sampling date.

- 2) Separately for each metal and site, the results for each of the twelve sampling dates was ranked from lowest to highest (1 - 12).
- 3) The probability of non-exceedance (percent) was determined for each of the 12 data points by dividing the rank by $n + 1$.
- 4) Using a log scale for the y-axis and a log probability scale for the x-axis, each of the twelve data points (y-axis) was plotted against the percent probability of non-exceedance (x-axis).
- 5) The log of each of the twelve results was calculated, and the mean and standard deviation was determined. The antilog of the mean (50th percentile), the mean plus three standard deviations (99.86 percentile), and the mean minus three standard deviations (0.14 percentile) were also plotted, and a line was drawn through the three points.
- 6) A straight horizontal line representing the WQS for the selected metal (ex. $5.6 \mu\text{g/L}$ for copper) was also plotted and a straight vertical line was plotted representing the 99.63 percentile (the required compliance frequency to meet the chronic WQS).
- 7) If the plotted line from step 4 crossed the WQS line at ≤ 99.63 percent, then the metal was predicted to violate the WQS for at least four days in a three year period.

Three wet weather sampling events were used to determine the effect of rainfall on the ambient concentrations of the four metals. Because the data did not pass the test for normality, the Mann-Whitney rank sum test (a nonparametric test) was used, instead of the more standard t-test, to test for significant differences ($\alpha \leq 0.05$) between the samples collected during a significant rainfall event ($\geq \frac{1}{4}$ inch of rainfall), and the ambient samples collected during dry weather periods. The tidal event data were not used in the statistical comparison of the rainfall data, because these data represented the worst case concentration, which would potentially bias the analysis.

Data from two sampling events were used to determine the effect of tidal cycles on the concentrations of the four metals. A one-way analysis of variance (ANOVA) was used to determine

if there were significant differences ($\alpha \leq 0.05$) between the four tidal events using the mean concentration of all five stations. Because the data did not pass the test for normality, the Kruskal-Wallis ANOVA on ranks (non-parametric test) was used to test for significance.

RESULTS

Tributary Water Column Surveys

Both dissolved and total-recoverable metals analyses were performed, but for purposes of assessing the probability of compliance with water quality criteria, only dissolved copper, nickel, and lead and total-recoverable mercury data were evaluated (Table 2). The results for copper and nickel collected from the Raritan River on September 20, 1995, were not considered to be acceptable, and were consequently not included in the analysis. This decision was made because the copper and nickel results for this sample were greater (by a factor of five to ten) than the other measurements made for the Raritan River station (Station 156) during the study. The batch of samples that contained this sample was processed and analyzed twice because quality control criteria were not met for the first analysis (low recoveries of the matrix spike and reference material samples). The QC data associated with the reprocessed batch were excellent, and these data were considered the best available for the entire batch of samples, but the copper and nickel data associated with this second analysis of the sample were much higher than all other observations, and appear to be artifacts of isolated sample contamination. To illustrate this point (see table below), for the first round of analysis (which did not pass quality control requirements), copper and nickel values for Station 156 were very close to those measured for the nearest station (Raritan Bay, Station 155). However, after reanalysis, the copper and nickel values for Station 156 were substantially higher than Station 155 or the first analysis.

ANALYSIS 1	COPPER ($\mu\text{g/L}$)	NICKEL
Station 155	0.61	0.60
Station 156	0.66	0.72
Percent Recovery	35.0	22.0

ANALYSIS II	COPPER	NICKEL
Station 155	1.94	2.44
Station 156	9.76	16.85
Percent Recovery	107.0	104.0

These results indicate that the September 20, 1995, sample for the Raritan River was contaminated during reprocessing or reanalysis. Consequently, these results are suspect and were not evaluated in this study to determine potential water quality criterion exceedances.

The measured ambient concentrations of copper and lead never exceeded their respective WQS at any of the locations, and were generally less than half of the 5.6 $\mu\text{g/L}$ WQS. The majority of the measured copper concentrations were in the 1 - 2 $\mu\text{g/L}$ range, with only the Raritan River, the Hackensack River, and the Passaic River rarely having somewhat higher dissolved copper concentrations (Figure 2). In the case of lead, all of the measured ambient dissolved concentrations were dramatically lower than the lead WQS (Figure 3). The measured nickel concentrations exceeded the WQS in the Hackensack River on June 15, 1995, and were within 2 $\mu\text{g/L}$ of the WQS in five other instances (Figure 4). Nickel concentrations were next highest in the Passaic River, although they were much lower than nickel concentrations in the Hackensack River. Nickel concentrations for the remaining sample stations were all in the 1 - 2 $\mu\text{g/L}$ range throughout the study.

Mercury levels did not exceed the WQS in Raritan Bay, but there were four occasions when the WQS was exceeded in the Raritan River. For Newark Bay and the Hackensack and Passaic Rivers collectively, the mercury WQS was exceeded on all but four sampling dates; Newark Bay had exceedances on 10 of 12 sampling dates, and both the Hackensack and Passaic Rivers had exceedances on 11 of 12 sampling dates (Figure 5). Both Newark Bay and the Hackensack River had mercury levels which greatly exceeded the WQS, and in four instances mercury levels in the Passaic River were 15 to 35 times higher than the WQS.

Log probability distributions were performed for each metal from each of the sites to determine the probability that the applicable WQS would be exceeded (Figures 6-25). The non-exceedance criterion (99.63 percent) was never predicted to be exceeded for copper or lead at any of the locations (Figures 6-10 and 16-20). For nickel, the non-exceedance criterion was predicted to be exceeded only in the Hackensack River (Figure 14), where the probability of not exceeding the 8.2 $\mu\text{g/L}$ criterion was 84 percent. For the Passaic River, the probability distribution indicated that the 8.2

$\mu\text{g/L}$ criterion was nearly projected to be exceeded, but that in fact the projected concentration at the 99.63 percentile was $8.09 \mu\text{g/L}$. With the exception of Raritan Bay, for all locations the probability was less than 96.63 percent that the $0.025 \mu\text{g/L}$ criterion for mercury would not be exceeded (Figures 21-25). The probabilities of not exceeding the criterion were 14 percent for Newark Bay, 18 percent for the Passaic River, 20 percent for the Hackensack River and 76 percent for the Raritan River. The raw data for both the dissolved and total recoverable copper, nickel, lead, and mercury are located in Appendix A.

Rainfall Influence

There were three rainfall events during which metals samples were collected. The date, amount of rainfall, and the duration of each of the rain events is as follows:

September 20, 1995; 1.24 inches; 65 hours
September 27, 1995; 0.86 inches; 42 hours
September 8, 1995; 0.60 inches; 24 hours

There were no significant differences between the ambient concentrations of the four metals measured during the rainfall events, and the concentrations measured during dry periods. For copper, nickel, and lead, the mean ambient concentration was actually lower during the rain events than during the dry periods; the mean concentrations of metals measured during the rainfall/dry periods were $1.691/1.776 \mu\text{g/L}$, $2.49/2.976 \mu\text{g/L}$, and $0.29/0.342 \mu\text{g/L}$, for copper, nickel, and lead, respectively.

For mercury, the mean concentrations measured during the rainfall events among the five sites were almost twice those measured during the dry periods ($0.126/0.065 \mu\text{g/L}$), although the differences in mercury concentrations between rainfall and dry periods were not statistically significant. To determine whether or not these two data sets were significantly different, the mercury data for the 12 events were ranked from highest to lowest concentration for each individual site (1-12). The data from each of the five sites was then considered to be a replicate, and the rank scores were then added for each of the 12 dates independently. This process determined the average rank for each of the 12 sampling dates. The average ranks for the three rain events, in chronological order, were 7.2, 5.6, and 7.2. With an average rank being six, it is evident that the rain events did not cause a statistically significant increase in the level of mercury. A Kruskal-Wallis one way

ANOVA on ranks was used to determine if there was a statistical difference in the rank scores for the 12 events. This statistical test determined that the differences in the median values among the 12 sampling dates were not great enough to exclude the possibility that the difference was due to random sampling variability ($P = 0.684$).

A Spearman rank order correlation was run between mercury concentrations and dissolved organic carbon (DOC), particulate carbon (PC), total organic carbon (TOC), and total suspended solids (TSS). For this test, the rank of mercury concentration was compared to the rank of the four variables independently (DOC, PC, TOC, and TSS). The Spearman test was used to determine if there was a correlation between the ranks; a correlation coefficient close to 1.0 indicating a strong positive relationship, while a correlation coefficient close to -1.0 indicating a strong negative relationship. The correlation coefficients for the four variables were 0.557, 0.559, 0.611, and 0.624 for DOC, PC, TOC, and TSS, respectively, indicating that there was a weak positive relationship between mercury concentrations and the concentrations of the four variables.

Tidal Cycle Influence

There were no statistically significant differences between the measured concentrations of the four metals for samples collected over a complete tidal cycle for both the August and October sampling dates. There were, however, several interesting trends between metal concentrations and tidal cycle that were apparent. Individually for copper, nickel and lead on both tidal cycle sampling dates, the mean concentration for all five sites combined was always highest during the low tide. In contrast, with the exception of the nickel sample collected in October, samples collected during high tide had the lowest concentrations of these same metals. The metals concentrations measured in samples collected during the ebb and flood tides generally fell between the low and high tide values. There was no relationship that was obvious between measured mercury levels and tidal cycle.

Comparison with 1991 Survey

The projected water quality exceedances based upon the present survey were compared to the worst case projected values for the four metals of interest based upon data collected in the 1991 survey (HydroQual 1995). For dissolved copper, the projected criterion exceedances were all less than the 1991 worst case projected values. For the Raritan, Hackensack, and Passaic Rivers this was

in contrast with the 1991 data for these sites; consequently, copper concentrations at these sites are no longer of concern. Both the Raritan and Newark Bay data from 1991 and 1995 were below the WQS for dissolved copper, consequently copper concentrations at these areas were never of concern. For dissolved nickel, the same areas that were of concern in 1991 continued to be areas of concern based upon the 1995 data; both the Hackensack and Passaic Rivers were areas of concern based upon both the 1991 and 1995 data. For dissolved lead, the data from all five sites using both the 1991 and 1995 data indicated there were no areas of concern. Based upon the 1995 data for total recoverable mercury, Raritan Bay changed from an area of concern to an area of no concern. The remaining four sites were in 1991, and continue to be, areas of concern for total recoverable mercury.

Sediment Survey

The sediment survey was conducted during the July 23 - 27 sample event. All four metals were analyzed from samples collected at the same five stations where the water samples were collected (Table 3). Copper levels in the sediments ranged from 66.9 - 176 $\mu\text{g/g}$; levels were lowest in the Raritan River and highest in the Passaic River. Nickel levels ranged from 22.9 - 53.1 $\mu\text{g/g}$; levels were lowest in the Raritan River and highest in the Passaic River. Lead levels ranged from 55.9 - 330 $\mu\text{g/g}$, with levels again lowest in the Raritan River and highest in the Passaic River. Sediment mercury concentrations were the most variable among the sites, with concentrations ranging from 0.076 - 330 $\mu\text{g/g}$. The concentrations were once again lowest in the Raritan River, and were highest in the Hackensack River.

Other Water Quality Data

Along with the metals analyses in both water and sediments, other water-quality parameters were measured including: dissolved organic carbon (DOC), particulate carbon (PC), particulate nitrogen (PN), total suspended solids (TSS), temperature (C), dissolved oxygen, pH, and salinity. These data are included in Appendices B, C, and D.

Suspended solids data were collected using both glass fiber filters and nucleopore filters. Although it is widely recognized that nucleopore filters produce more accurate data because of the influence of salt on the operation of glass fiber filters, both procedures were utilized to provide a basis for comparison with previously-collected data.

A Mann-Whitney rank sum test was used to test for significant differences between the TSS results using the glass fiber filters and the nucleopore filters. This test showed that the difference in the median values of the two groups was greater than would be expected by chance; there was a statistically significant difference in TSS results between the two filter types ($P < 0.001$). The median values for the glass fiber filters and the nucleopore filters were 29.2 and 18.0, respectively, illustrating that the glass fiber filters produced unrealistically high results.

DISCUSSION

In spite of the fact that a number of water quality criteria exceedances were projected for the New Jersey tributaries and Raritan and Newark Bays based upon the 1991 survey data (HydroQual 1991), the more comprehensive data set collected in 1995 demonstrated relatively few potential water quality criterion exceedances, with the exception of mercury. All copper values collected at all sites were well below the copper WQS, and as a consequence, there were no copper WQS exceedances projected for any of the water bodies that were sampled in this program. The magnitude of the difference between the WQS for lead and the measured ambient lead concentrations was the most dramatic of any of the metals measured, with concentrations generally ranging between 0.5 and 1.0 $\mu\text{g/L}$, compared to the lead WQS of 8.1 $\mu\text{g/L}$. Thus, lead is clearly not a water quality issue in any of the New Jersey water bodies evaluated in the present program.

Nickel concentrations were well below the nickel WQS (8.2 $\mu\text{g/L}$) for Raritan Bay, the Raritan River and Newark Bay, and the probability distributions for nickel at those sites indicated that the probability that the WQS for nickel will not be exceeded for four days more frequently than once every three years is greater than 99.63 percent. Therefore, nickel is not a water quality concern at those sites. The nickel probability distribution for the Passaic River (Figure 15) also showed that there was not a projected WQS exceedance for nickel, although the probability distribution indicated that the 8.2 $\mu\text{g/L}$ criterion approached a projected exceedance. In contrast, for the Hackensack River one of the samples contained a higher concentration of nickel than the WQS, and a meaningful number of the remaining samples contained nickel concentrations that were approaching the WQS. Thus, when the probability distribution was plotted for the Hackensack River, the data illustrated that WQS exceedances are likely at that site (Figure 14). This outcome is to be expected, given that one of the samples collected actually contained a higher concentration of nickel than the WQS.

For the most part, the mercury data were considerably different from the data collected for copper, lead and nickel. With the exception of Raritan Bay, where there were no measured or projected mercury WQS exceedances (Figures 5 and 21), there were both measured and projected WQS exceedances for mercury at all of the other sampling locations (Figures 5 and 22-25). In the case of the Raritan River, the measured and projected WQS exceedances were not dramatic, whereas for the remaining sites (Newark Bay, the Passaic River and the Hackensack River) measured concentrations typically exceeded the mercury WQS, sometimes by factors as high as 35 times the WQS. Naturally, these high measured concentrations resulted in very high probabilities of exceedance for mercury at those sites.

There has been much speculation since the 1991 Harbor study concerning the most likely source(s) of mercury to the Harbor complex. Much of the discussion has centered around the possibility that the atmosphere, in the form of both wet and dry deposition, is responsible for a large percentage of the unidentified mercury load to the Harbor. We believe that the mercury data collected in this study clearly illustrate that although there almost certainly is a base load of mercury entering the estuary atmospherically, the vast majority of the mercury in the water column of the New York/New Jersey Harbor and the associated New Jersey tributaries originates from non-atmospheric sources. And we believe that it is the site-to-site variability in the mercury data that provides the most compelling argument that the sources of mercury to the Harbor estuary are primarily non-atmospheric.

To illustrate this point, we believe it is reasonable to assume that the watersheds for the Passaic, Hackensack and Raritan Rivers are all generally under the influence of the same atmospheric inputs, and yet the measured ambient mercury concentrations from these sites differ by factors in excess of 300. If the atmosphere were responsible for these dramatic differences, then the site-to-site differences in atmospheric loads would be substantial, which we feel is unlikely in such a small geographic area. Conversely, if the estuary were receiving an atmospheric load that was responsible for a large portion of the unidentified load to the Harbor, then the measured ambient mercury concentrations would be much more uniform throughout the Harbor complex. That is not to imply that mercury is not entering the Harbor waters atmospherically, but rather that it is more reasonable to assume that the concentrations of mercury that were measured in Raritan River (0.00567-0.04223 $\mu\text{g/L}$) or Raritan Bay (0.00271-0.01233 $\mu\text{g/L}$) may be most representative of baseline mercury concentrations for the Harbor estuary resulting from atmospheric inputs, and that the dramatically

higher ambient mercury concentrations measured at the other locations in this study are the result of other sources, including mercury sediment cycling mechanisms.

Based on the water column and sediment data collected in this study, we believe it is reasonable to hypothesize that a very important source of mercury to the water column at the sites studied may be the sediments. Table 3 presents the mercury sediment data for each of the sites, and Figure 26 illustrates the relationship between measured sediment mercury and ambient water mercury concentrations, based on the median values for the ambient mercury data and the single sample results for the sediments. As Figure 26 clearly demonstrates, there is an obvious relationship between the measured sediment mercury concentrations and the water column mercury concentrations measured in this study; in both the Raritan River and Raritan Bay the sediment mercury concentrations were relatively low, as were the measured ambient mercury concentrations. In contrast, in Newark Bay, the Hackensack River and the Passaic River where the ambient mercury values were the highest, the mercury sediment concentrations were also high. We recognize that the relationship is not perfect (the Hackensack River sediment mercury concentration is higher than the Passaic River sediment mercury value, in contrast to the ambient mercury values), and that the mercury sediment database is limited (only one sample was collected and analyzed per site). Nevertheless, the relationship illustrated in Figure 26 is sufficiently clear to strongly suggest that the sediments may well be playing a role in influencing water column mercury concentrations throughout the Harbor estuary complex. We also recognize that the acid volatile sulfides (AVS) concentrations in the sediment samples (Table 3) suggest that the mercury in the sediments is sufficiently complexed so that it may not be available to the water column. However, because sediment resuspension and sediment exposure to aerobic conditions are phenomena that undoubtedly are important factors during the daily tidal cycles, we believe it is reasonable to hypothesize that the sediments may well be important sources of mercury to the water column. Another possibility (although probably less likely) is that the sediment mercury concentrations may be high because the sediments are acting as a sink for the current high water column concentrations, and that the mercury is entering the water column from point or nonpoint (other than sediments or the atmosphere) sources.

Unfortunately, the data collected in this study are not sufficient to definitively determine the magnitude or characteristics of the contributions of mercury from the sediments to the water column, or from the water column to the sediments, because this study was not designed to address that issue. In the first place, as stated above, only one sediment sample was collected from one site in each water body studied. A more robust sediment database would be required to gain a better perspective on the

distribution of mercury in the sediments throughout the Harbor. Secondly, the species of mercury that are present in both the sediments and the water column were not measured in this study (only total mercury was measured, a measurement that is directly affected by the suspended solids content of the sample), and mercury speciation work would be required to definitively determine the role that the sediments, anoxic microzones within aerobic sediments, and AVS may play in affecting mercury concentrations in the water column.

Under anaerobic conditions in sediments, methyl-mercury compounds can be created and released to the water column, and it is the organo-mercury compounds which are the most toxic, and which are responsible for the extremely low mercury WQS (0.025 $\mu\text{g/L}$ total recoverable mercury). Thus, it would be important to measure the species of mercury in both the water column and in the sediments to gain a clearer understanding of the relationship between sediment and water column mercury. Finally, because ambient mercury concentrations were not measured at multiple upstream locations (particularly in the Passaic and Hackensack Rivers), it is not possible to determine if the high measured ambient concentrations are a consequence of upstream inputs, local inputs, or mercury cycling from the sediments. In order to address this issue, additional upstream mercury sampling would be required to better understand this sediment/water column mercury relationship.

Another approach that could be used to gain an understanding of how sediment mercury may affect ambient water quality would be to measure the concentrations of the toxic species of mercury in marine organisms, either resident fish/shellfish or caged fish/shellfish. If the species of mercury that is present in the water column is the bioavailable (and therefore toxic) form, it will accumulate in the tissues of fish and shellfish. Thus, an investigation that focuses on mercury tissue concentrations, coupled with mercury speciation work in the water column, in the sediments, and in upstream samples would help provide the necessary information to understand the sediment water column interactions, and the biological significance of those interactions. However, in spite of the fact that there is much that is not known about the role of sediment mercury, the data presented in Figure 26 presents compelling evidence suggesting that a relationship exists between mercury in sediments and mercury in the water column.

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TABLE 1. SUMMARY OF PHASE I NEW JERSEY TRIBUTARY/HARBOR METALS SAMPLING SURVEYS

SAMPLING DATE (1995)	WATER QUALITY STATIONS	WATER QUALITY SAMPLE SETS	SEDIMENT STATIONS	SEDIMENT SAMPLE SETS
June 14 - 16	5	5	0	0
July 6	5	5	0	0
July 23 - 27	5	5	5	5
August 08 - 11 (tidal cycle)	5	20	0	0
August 25 - 26	5	5	0	0
September 13	5	5	0	0
September 20 (rainfall event)	5	5	0	0
September 26 - 28 (rainfall event)	5	5	0	0
October 17 - 18 (tidal cycle)	5	20	0	0
November 8 (rainfall event)	5	5	0	0
November 30	5	5	0	0
December 13	5	5	0	0

TABLE 3. CONCENTRATION OF SELECTED METALS (COPPER, NICKEL, LEAD, MERCURY) IN SEDIMENT AT FIVE SITES FOR PHASE I SAMPLING

SITE	ANALYTE (µg/g)								
	Copper	SEM ¹ Copper	Nickel	SEM ¹ Nickel	Lead	SEM ¹ Lead	Mercury	SEM ¹ Mercury	AVS ²
Raritan Bay (155)	142	56.8	39.7	6.78	190	142	0.826	0.0690	492
Raritan River (156)	66.9	21.0	22.9	2.87	55.9	38.1	0.076	0.0116	102
Newark Bay (301)	105	12.7	35.1	4.98	133	92.4	2.68	0.00953	1060
Hackensack River (303)	147	9.44	48.5	6.63	150	85.1	4.81	0.0339	2540
Passaic River (306)	176	80.0	53.1	8.96	330	236	3.24	0.0426	276

¹ Simultaneously Extracted Metals.

² Acid Volatile Sulfides.